

SHORT
COMMUNICATIONS

Catalytic α -Elimination of β -Oxo- α -chloroaldehydes Hydrazones

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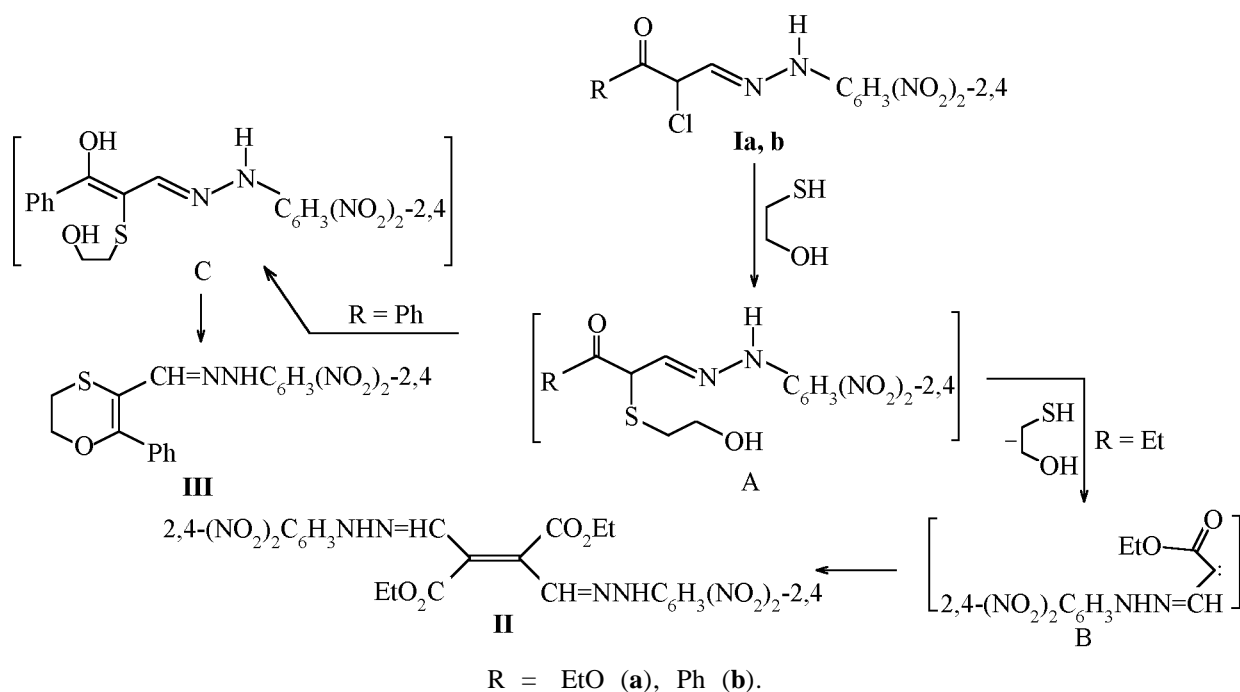
We showed formerly [1] that β -oxo- α -chloroaldehydes hydrazones when treated with sodium methylate underwent an uncommon α -elimination followed by dimerization.

During the investigation of reaction between α -chlorocarbonyl compounds **I** with mercaptoethanol we observed that hydrazone **Ia** underwent catalytic α -elimination affording compound **II**, and hydrazone **Ib** was involved in cyclocondensation resulting in heterocycle **III**.

The structure of compounds **II**, **III** was proved by ^1H and ^{13}C NMR spectroscopy.

The quite dissimilar course of two reactions may be rationalized taking into consideration the structural features of the presumed intermediates A arising as a result of nucleophilic substitution of chlorine atom.

It is known that in compounds of $\text{PhC(O)CH}_2\text{X}$ type (where X is an electron-acceptor substituent) the enol form content amounts to 90% whereas in substances with an ethoxycarbonyl group, $\text{EtOC(O)CH}_2\text{X}$, the



enol content is in the range of 7.7×10^{-3} – $2.5 \times 10^{-1}\%$ [2].

This fact suggests that benzoyl-substituted intermediate A through enol form C easily cyclizes into

heterocycle **III** whereas ethoxycarbonyl-containing intermediate A by acid proton elimination presumably through carbene B transforms into polyfunctional compound **II**.

The results of this study unambiguously indicate that mercaptoethanol is a catalyst of the α -elimination process. Actually we proved experimentally that ethoxycarbonyl-substituted hydrazone in the presence of catalytic amounts of mercaptoethanol, 1,2-ethanedithiol, and 2-propanethiol suffered "dimerizational α -elimination."

It should be noted that α -elimination is fairly rare event [3, 4]. Among aryl and alkyl halides relatively small number of examples is known [5, 6].

Thus for the first time a catalytic α -elimination of functionally substituted α -halocarbonyl compounds was discovered.

Reaction of ethyl 3-(2,4-dinitrophenylhydrazono)-2-chloropropanoate with mercaptoethanol.

(a) To a solution of 3 g (9 mmol) of hydrazone **Ia** in 15 ml of anhydrous DMSO at 15°C while stirring was added dropwise 0.7 g (9 mmol) of mercaptoethanol in 5 ml of DMSO. The separated precipitate of compound **II** was filtered off and recrystallized from DMSO, yield 85%, mp 240–242°C (publ. 240–242°C [1]). Melting point determination on a sample mixed with an authentic substance showed no depression.

(b) To a solution of 3 g (9 mmol) of hydrazone **Ia** in 15 ml of anhydrous DMSO at stirring was added dropwise 0.9 mmol of mercaptoethanol or 1,2-ethanedithiol or 2-propanethiol in 2 ml of DMSO. The separated precipitate of compound **II** was filtered off and recrystallized from DMSO, yield 80%, mp 240–242°C.

2-Phenyl-5,6-dihydro-1,4-oxathiine-3-carbaldehyde 2,4-dinitrophenylhydrazone (III). A solution of 3 g (8.28 mmol) of hydrazone **Ib** in 30 ml of anhydrous ethyl acetate was stirred at heating to ~50°C till hydrazone **Ib** completely dissolved. Then a solution of 0.65 g (8.28 mmol) of mercaptoethanol

in 5 ml of ethyl acetate was added dropwise. The reaction mixture was boiled for 5 h, then it was cooled to room temperature, and 3 h later the separated precipitate of compound **III** was filtered off, washed with ethyl acetate and acetone, and recrystallized from DMSO. Yield 2.9 g (84%), mp 214–216°C. IR spectrum, ν , cm^{-1} : 1470 (C=N), 2880 (NH_2^+), 3260 (NH). ^1H NMR spectrum [$(\text{CD}_3)_2\text{SO}$], δ , ppm: 3.23 m (2H, SCH_2), 4.15 m (2H, 2OCH_2), 7.41 s (5H, Ph), 8.39 s (1H, CH=N), 11.75 s (1H, NH). ^{13}C NMR spectrum [$(\text{CD}_3)_2\text{SO}$], δ , ppm: 25.00 (SCH_2), 67.10 (OCH_2), 95.80 (=C-S), 107.50, 117.50, 123.00, 135.00, 144.00 (Ar), 127.50, 128.30, 129.75, 136.50 (Ph), 148.00 (CH=N), 157.50 (O-C=). Found, %: Cl 8.99; N 13.57. $\text{C}_{17}\text{H}_{15}\text{ClN}_4\text{O}_5\text{S}$. Calculated, %: Cl 8.40; N 13.25.

IR spectra were recorded on UR-20 instrument. ^1H NMR spectra were registered on spectrometer Tesla BW-567 at 100 MHz, reference HMDS. ^{13}C NMR spectra were measured on spectrometer Bruker MSL-400 at 100.6 MHz, reference HMDS.

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